SOME COORDINATION COMPOUNDS OF COBALT AND CHROMIUM WITH ORGANIC DIAMINES

BY

JOE BOEHM WORK

A.B., Wittenberg College, 1938
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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1942

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It is well known that ethylenediamine and metal salts form a wide variety of coördination compounds which owe their stability to the presence of five-membered chelate rings. Similar compounds having larger rings, however, are both more difficult to prepare and less stable than those containing ethylenediamine or its derivatives.

The present study was designed to examine the coördinating ability of diamines which would give rise to chelate rings of six or more atoms. In the course of the investigation it was noted that Bjerrum[1] had used activated charcoal to catalyze the formation of hexammine cobaltic chloride and triethylenediamine cobaltic chloride. It has now been shown that many other reactions in the field of coördination compounds are subject to catalysis by such materials of large surface area as activated carbon, Raney nickel, and silica gel. The fundamental type of reaction catalyzed is the entrance of nitrogen (of either nitro or amine groups) into the coördination sphere of a metal ion. The function of the catalyst is probably to adsorb preferentially certain ions or molecules which subsequently react due to the high concentration on the surface of the catalyst.

It has been shown that activated carbon catalyzes the following reactions:

1—*trans* $[Co\ en_2\ Cl_2]Cl + 2\ NaNO_2 \rightarrow [Co\ en_2(NO_2)_2]Cl + 2\ NaCl$

2—*levo-cis* $[Co\ en_2\ Cl_2]Cl + \text{excess}\ NaNO_2 \rightarrow$ *dextro-cis* $[Co\ en_2(NO_2)_2]NO_2 + 3\ NaCl$

3—*trans* or *cis* $[Co\ en_2\ Cl_2]Cl + \text{excess}\ NH_4OH \rightarrow$ *trans* (+ *cis*) $[Co\ en_2(NH_3)_2]Cl_3 + H_2O$

4—*dextro-cis* $[Co\ en_2(NH_3)Cl]Cl_2 + \text{excess}\ NaNO_2 \rightarrow$ *dextro-cis* $[Co\ en_2(NH_3)(NO_2)]Cl_2 + NaCl$

5—*cis* $[Co\ en_2(NH_3)Cl]Cl_2 + \text{excess}\ NH_4OH \rightarrow$ *trans* (+ *cis*) $[Co\ en_2(NH_3)_2]Cl_3 + H_2O$

6—$[Co\ en_2(NH_3)_2]Cl_3 + \text{excess}\ NaNO_2 + \text{heat} \rightarrow 2NH_3 + [Co\ en_2\ (NO_2)_2]NO_2$

7—$4\ CoCl_2 + 10\ tn + 2(tn{\cdot}2HCl) + O_2 \rightarrow 4\ [Co\ tn_3]Cl_3 + 2\ H_2O$

8—$4\ CoCl_2 + 10\ dan + 2\ (dan{\cdot}2HCl) + O_2 \rightarrow 2\ H_2O + 4\ [Co\ dan_3]Cl_3$

9—$CrCl_3{\cdot}6H_2O + 3\ en + \text{heat} \rightarrow [Cr\ en_3]Cl_3 + 6\ H_2O$

10—$[Co\ en_2\ Cl_2]Cl + tn \rightarrow [Co\ en_2\ tn]Cl_3$

11—$[Co\ en_2\ Cl_2]Cl + \text{diabip} \rightarrow [Co\ en_2\ \text{diabip}]Cl_3$

12—$[Co\ en\ tn\ Cl_2]Cl + dan \rightarrow [Co\ en\ tn\ dan]Cl_3$

13—$[Co(NH_3)_5Cl]Cl_2 + NH_4OH \rightarrow [Co(NH_3)_6]Cl_3 + H_2O$

14—$Na_3[Co(NO_2)_6] + 3NH_3 \rightarrow [Co(NH_3)_3\ (NO_2)_3] + 3\ NaNO_2$

15—$NH_4[Co(NH_3)_2(NO_2)_4] + NH_3 \rightarrow [Co(NH_3)_3\ (NO_2)_3] + NH_4NO_2$

16—$[Co(NH_3)_6]Cl_3 + H_2O + \text{heat} \rightarrow Co(OH)_3 + Co(OH)_2 + NH_3 + NH_4Cl$

17—$[Co(NH_3)_6]Cl_3 + 3\ NaNO_2 + \text{heat} \rightarrow 3\ NaCl + 3\ NH_3 + [Co(NH_3)_3\ (NO_2)_3]$

(In the preceding equations "en" represents ethylenediamine, "tn" designates trimethylenediamine, "dan" stands for diaminoneopentane, and "diabip" refers to 2,2′-diaminobiphenyl.)

The reactions cited above were used as the bases for the development of methods for the preparation of such luteo type coördination compounds as $[Co\ tn_3]Cl_3$, $[Co\ dan_3]Cl_3$, $[Co\ en_2\text{-}tn]Cl_3$, and $[Co\ en\ tn\ dan]Cl_3$. In studying the properties of these compounds it was observed that $[Co\ tn_3]Cl_3$ and $[Co\text{-}dan_3]Cl_3$ have an anomalous pinkish-yellow color instead of the orange shade that would be expected. The only comparable case that has been recorded is that of tri-[*trans* cyclopentylenediamine] cobaltic chloride which Jaeger[2] prepared. As with this latter salt, the iodide of the $[Co\ tn_3]^{+++}$ series has the normal orange color. These facts have been discussed in the light of the presence of six-membered rings.

The use of charcoal has been shown to make possible several improvements in the methods for the preparation of [Cr en_3]Cl_3, [Co $en_2(NO_2)_2$]Cl, [Co $en_2(NH_3)_2$]Cl_3, and [Co en_2 diabip]Cl_3.

Werner[3] has reported many reactions using [Co en_2 Cl_2]Cl as starting material. Included in this thesis is a chart which summarizes about twenty-five such reactions and also shows several examples of the catalytic ability of activated carbon.

Catalysis by charcoal was also used as a basis for an unsuccessful search for Walden Inversions in the reactions of resolved *cis* [Co en_2 Cl_2] Cl and *cis* [Co $en_2(NH_3)$ Cl]Cl_2 with sodium nitrite and ammonium hydroxide.

The presence of activated charcoal has been shown to catalyze the formation of [Co en_3]Cl_3 by disproportionation of [Co-en_2 Cl_2]Cl in aqueous solutions containing methyl amine, isopropyl amine, aniline, pyridine, or decamethylenediamine. The suggestion has been made that avoidance of aqueous solutions might eliminate this reaction. These disproportionation reactions represented failures to replace both chloro groups from [Co en_2-Cl_2]Cl. Hexamethylenediamine produced no disproportionation, but it could not be made to form a nine-membered chelate ring. The only success attained in efforts to obtain a ring having more than six members was the preparation of [Co en_2 diabip]Cl_3 which has been reported by Middleton[4]. In this case the positions of the amine groups are sufficiently limited by the rather rigid biphenyl structure that coördination with cobalt can occur. Attempts to prepare [Co en tn diabip]Cl_3 from [Co en tn Cl_2]Cl by methods similar to those used to obtain [Co en tn dan]Cl_3 and [Co en_2 diabip]Cl_3 did not succeed.

Methods were developed for the preparation of *trans* [Co tn_2-Cl_2]Cl, [Co dan_2 Cl_2]Cl, and [Co en tn Cl_2]Cl. These compounds were compared with *trans* [Co en_2 Cl_2]Cl and the differences in properties were discussed. Grinding these dichloro compounds with moist silver carbonate results in the formation of the corresponding carbonato compounds. Treatment of the carbonato salts with a solution of hydrogen chloride in a mixture of alcohol and ether yields the *cis* dichloro compounds. *Cis*

[Co tn_2 Cl_2]Cl and *cis* [Co dan_2 Cl_2]Cl rearrange to the *trans* form in the solid state, whereas *cis* [Co en tn Cl_2]Cl is stable.

Werner and Lindenberg[5] found *trans* [Co tn_2 Cl_2]Cl to change from green to purplish-red almost immediately upon dissolving in water. This reaction was found to occur with equal rapidity in the case of *trans* [Co dan_2 Cl_2]Cl, but more slowly for *trans* [Co en tn Cl_2]Cl. It was concluded that this color change is due to the formation of *trans* chloro aquo or diaquo salt rather than of *cis* dichloro salt, since the latter was so extremely unstable.

Among the other new compounds that have been prepared are [Co tn $(NH_3)(NO_2)_3$], [Co $tn_2(NH_3)Cl]Cl_2$, [Co $tn_2(NH_3)_2]Cl_3$, [Co dan_2 CO_3]Cl, [Co en tn $(NO_2)_2]NO_2$, [Co-en $tn(NH_3)Cl]Cl_2$, and [Co en $tn(NH_3)_2]Cl_3$.

A method has been described for the determination of ammonia content of coördination compounds which also contain diamines.

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VITA

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